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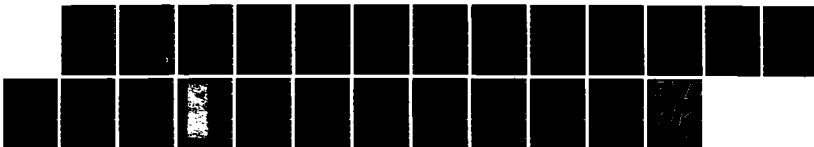
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Bethesda, Maryland 20084

THE INFLUENCE OF INCUBATION TIME ON THE PASSIVE
FILM BREAKDOWN OF ALUMINUM ALLOYS IN SEAWATER

by

Denise M. Aylor and Patrick J. Moran

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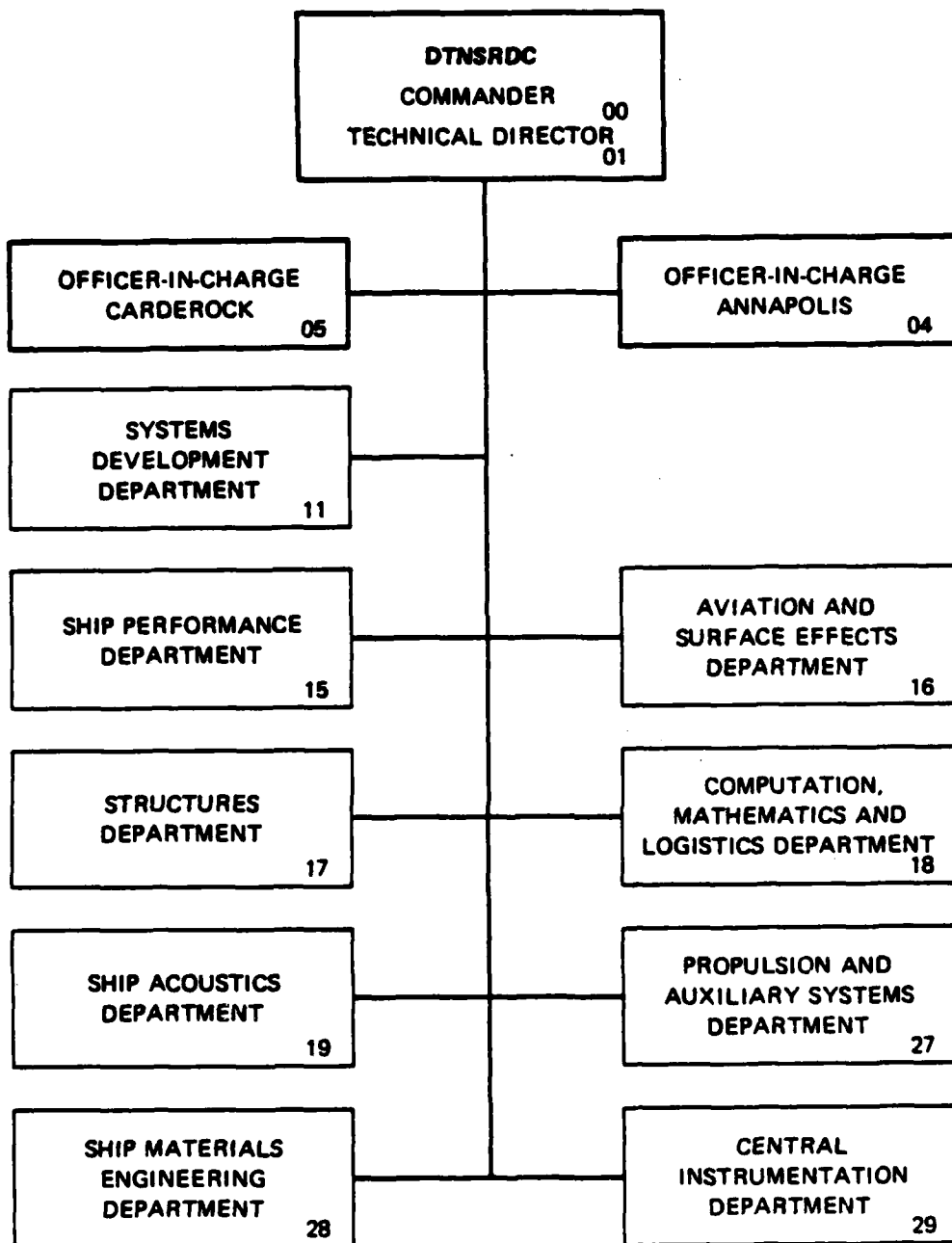
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method for obtaining E_{rp} after minimal pit growth or surface damage. Cyclic anodic polarization can also be used for determining a representative repassivation potential if surface damage subsequent to pit initiation is minimized.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CAP	Cyclic Anodic Polarization
°C	Degree Celsius
cm ²	Square centimeter
E _{bd}	Breakdown Potential
E _{corr}	Corrosion Potential
E _{rp}	Repassivation Potential
μA	Microampere
mA	Milliampere
PPR	Pit Propagation Rate
SCE	Saturated Calomel Electrode
V	Volt

ABSTRACT

Potential-controlled electrochemical methods were used to characterize the pitting behavior of 6061 alloy aluminum in synthetic ocean water. Irreproducible breakdown potentials (E_{bd}) and reproducible repassivation potentials (E_{rp}) were determined from cyclic anodic polarization (CAP). Reproducible breakdown and repassivation potentials were found from the quasi-stationary anodic polarization method; however, the breakdown potential values were shifted in the electronegative direction relative to the CAP method due to the allowance of a longer incubation time. These results support the theory that with sufficient incubation time, pit initiation and propagation will occur at potentials at or slightly above the repassivation potential, and that the repassivation potential value is the only characteristic potential for aluminum. The quasi-stationary anodic polarization method used for E_{rp} determination provides a reproducible electrochemical method for obtaining E_{rp} after minimal pit growth or surface damage. Cyclic anodic polarization can also be used for determining a representative repassivation potential if surface damage subsequent to pit initiation is minimized.

ADMINISTRATIVE INFORMATION

This work was authorized and funded by Work Unit 2813-420, "Metal Matrix Corrosion Control." The program is sponsored by Dr. J. Foltz, Naval Surface Weapons Center (Code R32), Program Element 62761N, Task Area RS61544. The work was performed in the Marine Corrosion Branch under the supervision of Mr. A.G.S. Morton.

INTRODUCTION AND BACKGROUND

Corrosion of aluminum-base alloys in chloride environments occurs predominantly by localized attack. This fact has been well documented in the literature.^{1,2*} A variety of electrochemical methods have been applied to the study of pitting processes for aluminum and other passive film-forming alloys in chloride environments. One common method is cyclic anodic polarization (CAP)**, governed by ASTM G61-78.³ Two distinctly different potentials are obtained from this test and are designated as the breakdown potential, E_{bd} and the repassivation potential, E_{rp} . E_{bd} is defined as the potential at which surface film breakdown occurs and it is indicated

*A complete listing of references is given on page 15.

**Definitions of abbreviations are given on page iv.

by a rapid increase in current. E_{rp} is defined as the potential at which the active surface repassivates after film breakdown and potential reversal. The repassivation is observed as a rapid decrease in current.⁴

Controversy continues over the significance of the breakdown potential determined from cyclic anodic polarization and as to whether two characteristic potentials truly exist. Also, there is concern about the reproducibility of the repassivation potential by this method.⁵ Numerous researchers⁵⁻⁸ have reported poor reproducibility for E_{bd} determined from CAP, attributing the irreproducibility to the fact that this potentiodynamic method significantly decreases the time available for the initiation of pitting. The existence of a pit incubation period (necessary before initiation) has been frequently cited in the literature.⁹⁻¹³ The incubation period for pit initiation is influenced by the environment and the structure and composition of the passive film, and it is also highly dependent on the applied potential. Work by Schwenk⁹ on 18/10 chromium-nickel steel and by Szklarska-Smialowska and Janik-Czachor¹⁰ on a 13 Cr-Fe alloy showed that the incubation time is substantially reduced as the applied potential is shifted in the electropositive direction. Because of this dependence of pit initiation on an incubation period, the scan rate used in potential-controlled electrochemical tests markedly influences the resultant E_{bd} . Leckie¹⁴ reported that for 304 stainless steel, the measured critical breakdown potential varied over 280 mV with a variation in scan rate over three orders of magnitude. The E_{bd} shifted in the electropositive direction as the scan rate increased. This combined effect of scan rate and incubation time on the measured E_{bd} is depicted in Figure 1.

Based on the above discussion, it could be argued that the two distinct potentials indicated by cyclic anodic polarization occur only as a result of an insufficient incubation time for pitting and that the true E_{bd} is equivalent to E_{rp} . In other words, only one characteristic potential exists. This argument will be developed further in the report for an aluminum alloy in seawater. Broli and Holtan¹² have presented a similar argument for pure aluminum in 3% sodium chloride solution.

Regarding the reproducibility of the repassivation potential, research by Wilde⁵ found that the E_{rp} as determined from cyclic anodic polarization is not a unique parameter. Wilde's research on 430 stainless steel in 1M sodium chloride solution showed that as the degree of pit propagation allowed before scan reversal was increased, the E_{rp} value shifted in the electronegative direction. The variation seen in E_{rp} results from changes in solution chemistry within the pit cavity,

caused by hydrolysis of corrosion products and chloride ion buildup as the pit propagates. With increased pit propagation repassivation becomes more difficult, and consequently the E_{rp} is shifted to a more electronegative value.

Various investigators have developed other potential-controlled methods to overcome the disadvantages of the CAP test. Pessall and Liu¹⁵ utilized a potentiostatic "scratch method" to eliminate the pit incubation period and to determine a reproducible E_{rp} after minimal pit growth. In this test, a specimen is scratched to initiate pitting while being potentiostatically controlled. If the surface repassivates, the specimen is below E_{rp} . If no repassivation occurs, the specimen is above E_{rp} . One disadvantage to this technique is that the initiation sites are determined by the scratch location rather than by the natural breakdown sites. The extent to which this influences the measured E_{rp} has not been determined. Also, Syrett¹⁶ developed a pit propagation rate (PPR) method to determine E_{rp} after minimal pit growth and to estimate the rate of pit propagation at potentials held between E_{bd} and E_{rp} . This method combines both potentiostatic and potentiodynamic techniques to yield useful data regarding pit propagation rates.

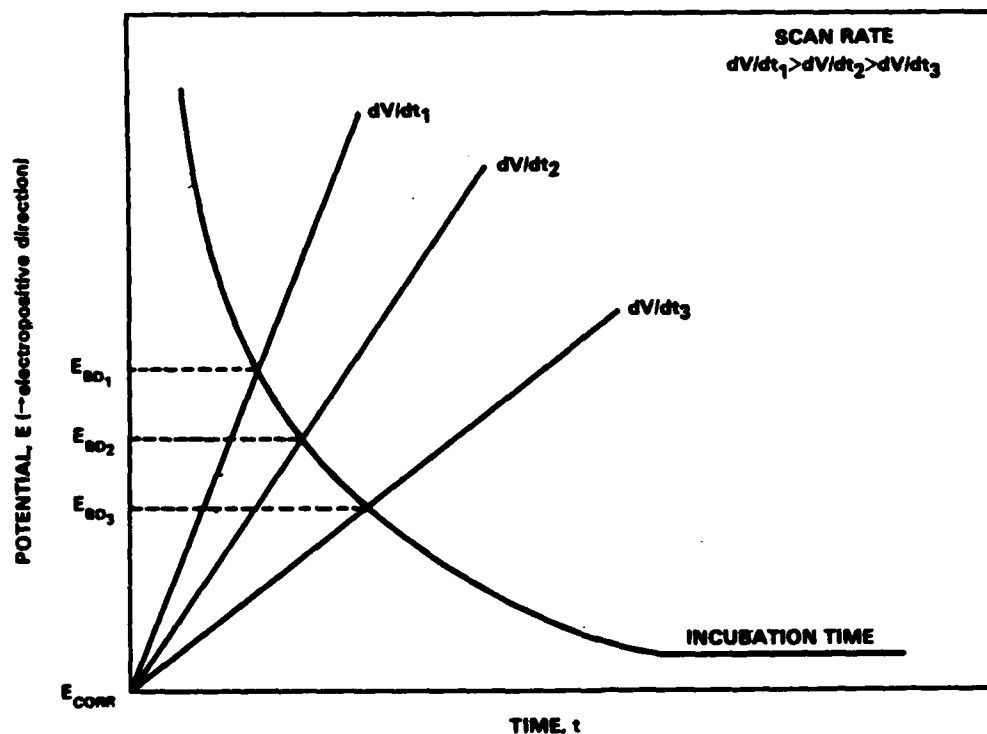


Figure 1 - Schematic Illustration of the Influence of Scan Rate on the Measured Breakdown Potential, E_{bd}

The purpose of the research reported herein was to characterize the pitting of 6061 alloy aluminum in synthetic ocean water through application of cyclic anodic polarization, quasi-stationary anodic polarization,¹⁷ and potentiostatic polarization. These methods will be compared, and the efficacy of the CAP test will be addressed, based on the electrochemical test results obtained.

EXPERIMENTAL PROCEDURE

A detailed description of each test method used in this investigation is given below. All experiments were conducted in ASTM ocean water, prepared according to ASTM Standard D1141-75.¹⁸ Specimens consisted of wrought 6061-T6 Al and powder metallurgy (PM) 6061 Al. Previous work by the authors⁸ showed that the electrochemical polarization behavior of both materials was essentially identical. Each specimen was mounted to expose a 2 cm² face. Equipment utilized included a Princeton Applied Research (PAR) Model 173 Potentiostat, a PAR Model 175 Programmer, and a PAR Model RE0074 X-Y Recorder or a Linseis Strip Chart Recorder. Specimens were allowed to reach a stable corrosion potential, measured relative to a saturated calomel reference electrode (SCE), in deaerated, ambient temperature (21-27°C) ocean water before the testing began. This typically required 2-4 days.

CYCLIC ANODIC POLARIZATION

CAP testing was conducted similarly to the procedure in ASTM Standard G61-78. Specimen immersion time prior to testing was typically longer than one hour to achieve a more stable E_{corr} and the maximum current density reached before scan reversal ranged from 1 to 5 mA/cm² to vary the extent of surface damage. After the corrosion potential was stabilized, the specimen was scanned in the electropositive direction at a 0.1 mV/s scan rate until a breakdown potential, E_{bd} , was observed. The scan was reversed when the current density exceeded 1 mA/cm² but before surpassing 5 mA/cm² and continued at the same rate until this electronegative direction scan crossed the original electropositive direction curve. This crossover point is the repassivation potential, E_{rp} .

QUASI-STATIONARY ANODIC POLARIZATION METHOD

The quasi-stationary anodic polarization method consisted of two separate tests, the first for determining the repassivation potential and then a second test utilizing the obtained E_{rp} value to determine a breakdown potential. Experimental procedures followed for E_{rp} determination are contained in ASTM F746-81¹⁹ and a graphical display of the test procedure is shown in Figure 2. This test begins by applying a +0.8 V versus SCE potential to the specimen to stimulate pitting. Once the current density exceeds $500 \mu\text{A}/\text{cm}^2$ at the +0.8 V potential, the potential is then immediately shifted to E_{corr} and the current monitored for 15 minutes. Low or decreasing currents (e.g. $<1 \mu\text{A}/\text{cm}^2$) signify pit repassivation whereas continuous increases or large fluctuations in current (e.g. $>1 \mu\text{A}/\text{cm}^2$) denote pit propagation. Assuming that pit repassivation occurs during this 15 minute period at E_{corr} the pit stimulation potential of +0.8 V versus SCE is applied again and the return potential is then shifted to a value 0.050 V electropositive to E_{corr} and the current monitored for 15 minutes. The test continues alternating between the +0.8 V potential and a return potential, shifting this return potential in the electropositive direction by 0.050 V for each interval. Test termination takes place when the return potential maintains an active surface after pit stimulation rather than promoting repassivation. E_{rp} is then designated as the most electropositive potential at which pit repassivation occurs after pit initiation.

A quasi-stationary anodic polarization procedure for E_{bd} determination was developed by the authors. This method is depicted in Figure 3 and consisted of the following steps:

1. Monitor the current for a minimum of ten minutes at an applied potential between E_{corr} and E_{rp} (as determined from the previously described method). Currents at this potential should be low ($10 \mu\text{A}/\text{cm}^2$ or less) and stable;
2. Apply a potential 0.025 V electropositive to the previously determined E_{rp} value. Monitor the current for a minimum of ten minutes;
3. Apply a preselected potential 0.025 V electropositive to the potential applied in step 2. Monitor the current for a minimum of ten minutes;
4. Continue alternating between the applied potential in step 2 and a preselected potential 0.025 V electropositive to the previous preselected potential. The rationale for alternating between the low (more electro-negative) and successively higher potentials is that pitting, once initiated, will be readily observed (by increasing current) at the low

- potential. Current values of $10 \mu\text{A}/\text{cm}^2$ or less at the applied potentials indicate that the breakdown potential has not yet been reached;
5. Terminate the test when the current continues to increase at the pre-selected potential and then stays high (greater than $100 \mu\text{A}/\text{cm}^2$) upon return to the potential in step 2;
 6. E_{bd} is conservatively designated as the potential 0.001 V electropositive to the last preselected potential where the current remained low.

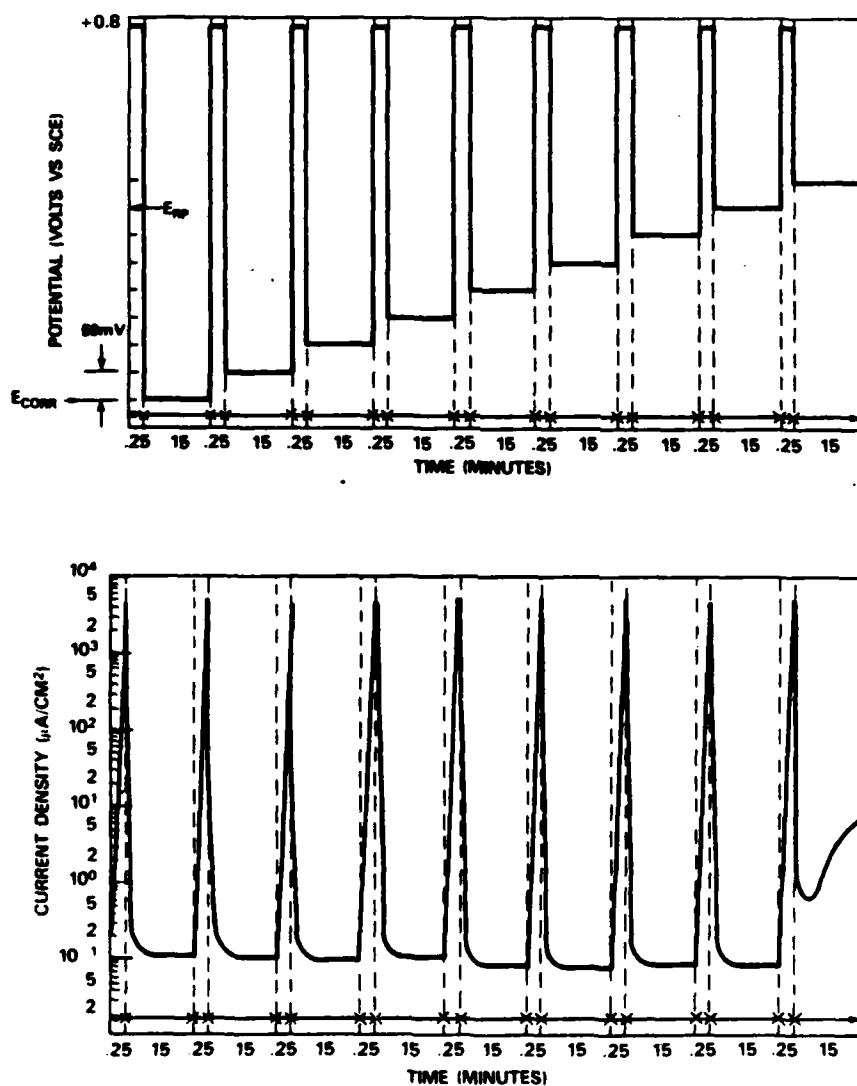


Figure 2 - Quasi-Stationary Anodic Polarization Method for E_{Rp} Determination (ASTM F746-81)

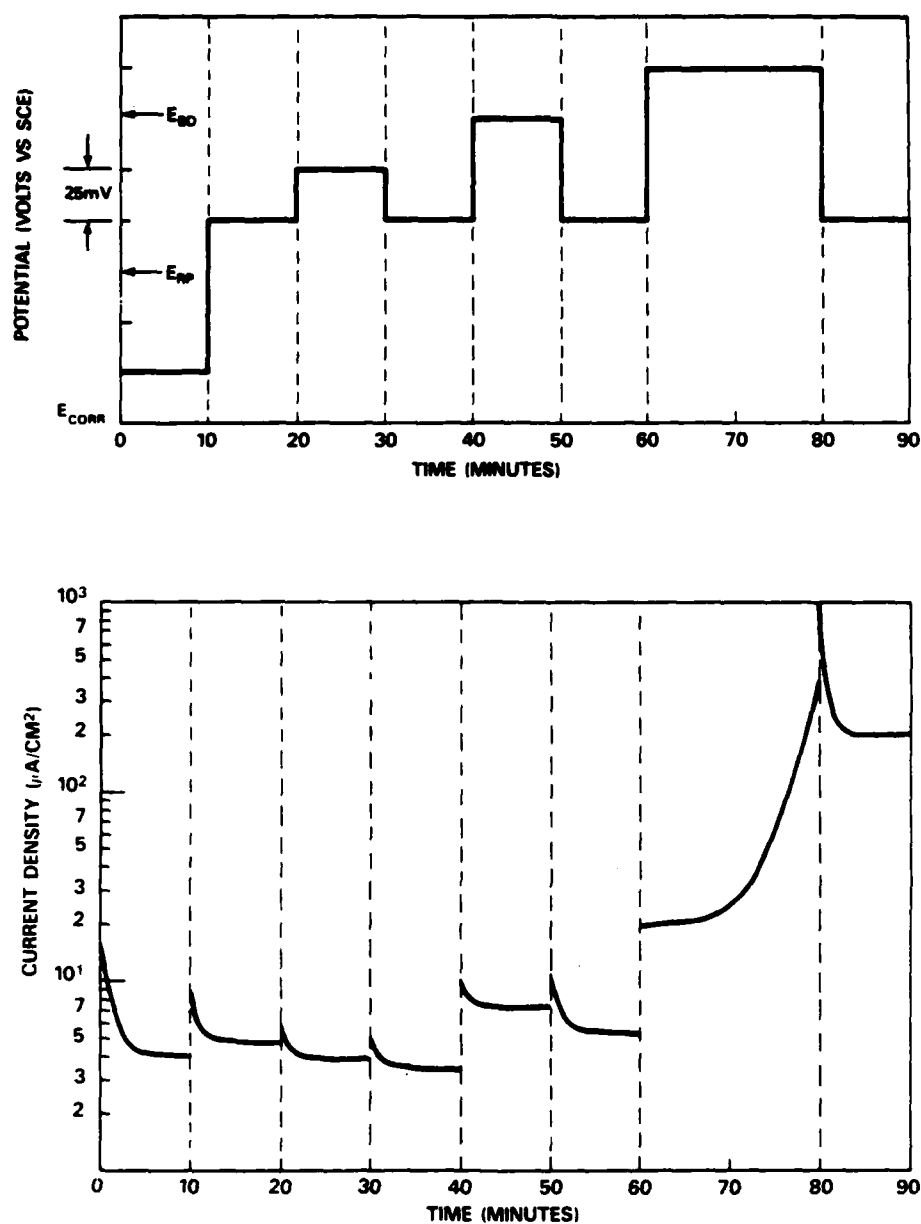


Figure 3 - Quasi-Stationary Anodic Polarization Method for E_{bd} Determination

POTENTIOSTATIC POLARIZATION

Potentiostatic polarization tests were conducted on three PM6061 Al specimens. Specimens were held at a potential of -0.650 V versus SCE and the current monitored for thirty minutes. These tests were done for comparison with the quasi-stationary anodic polarization method.

RESULTS AND DISCUSSION

Figure 4 presents the CAP results for PM6061 Al and 6061-T6 Al (from reference 8). The solid curves represent a range of potential and current density values based on three PM6061 Al specimens tested. The dashed curves represent a range of values for four 6061-T6 Al specimens. The shaded areas highlight the range of E_{bd} and E_{rp} values for both 6061 Al alloy forms. The measured corrosion potentials exhibited scatter because the extent of deaeration varied. Irreproducibility in the breakdown potential for both 6061-T6 Al and PM6061 Al is clearly evident. The repassivation potential is a much more reproducible parameter for each material. The E_{rp} range for PM6061 Al is slightly electronegative to the E_{rp} range for 6061-T6 Al due to an increased amount of pit propagation, as previously discussed. Note the higher currents subsequent to breakdown for the PM alloy relative to the wrought alloy.

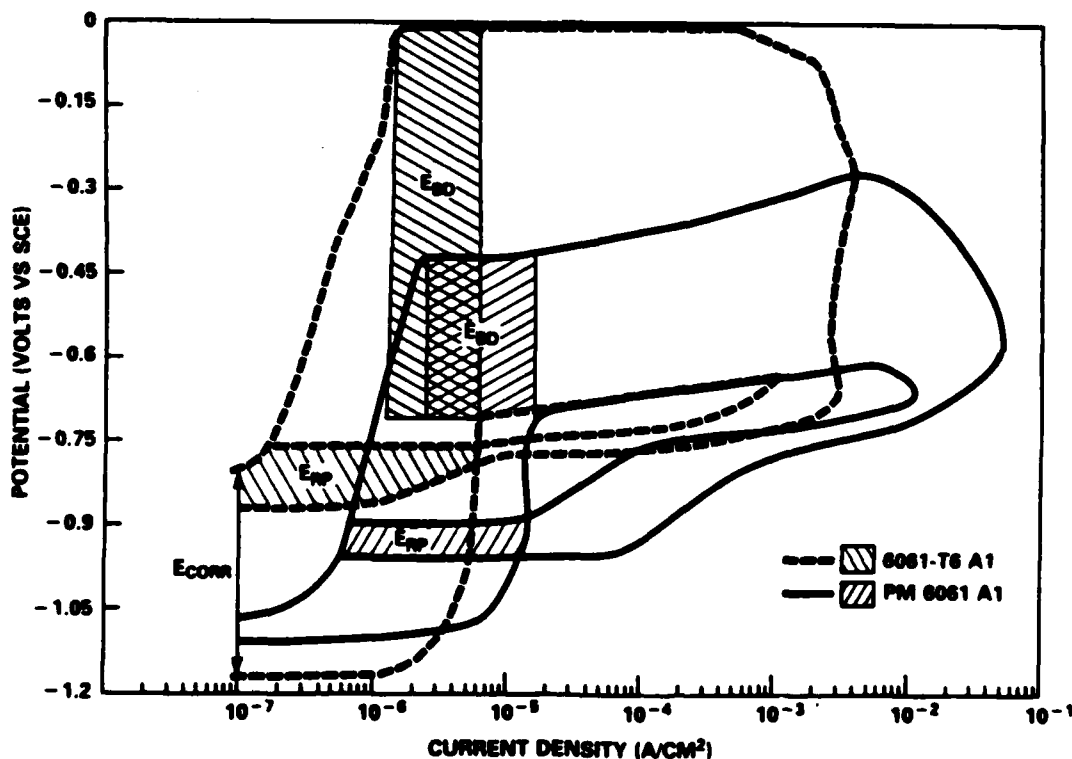


Figure 4 - Cyclic Anodic Polarization Data for 6061-T6 Al and PM6061 Al (Reference 8)

Figure 5 compares the repassivation potentials obtained from cyclic anodic polarization with those determined using the quasi-stationary anodic polarization method (ASTM F746-81). Each point represents a single test. Repassivation potentials determined using the quasi-stationary anodic polarization method were very reproducible. All specimens tested displayed a E_{rp} at -0.750 V versus SCE except for one PM6061 Al specimen where E_{rp} was -0.850 V versus SCE. This E_{rp} determination method yields a repassivation potential for 6061 aluminum after minimal surface damage (i.e. minimal pit growth), which avoids the complications in reproducibility of E_{rp} discussed by Wilde.⁵ The SEM photographs in Figure 6 compare the minimal surface damage on a 6061-T6 Al specimen after E_{rp} determination by the quasi-stationary anodic polarization method with the more penetrating pits which were typical of 6061-T6 Al surfaces after E_{bd} determination.

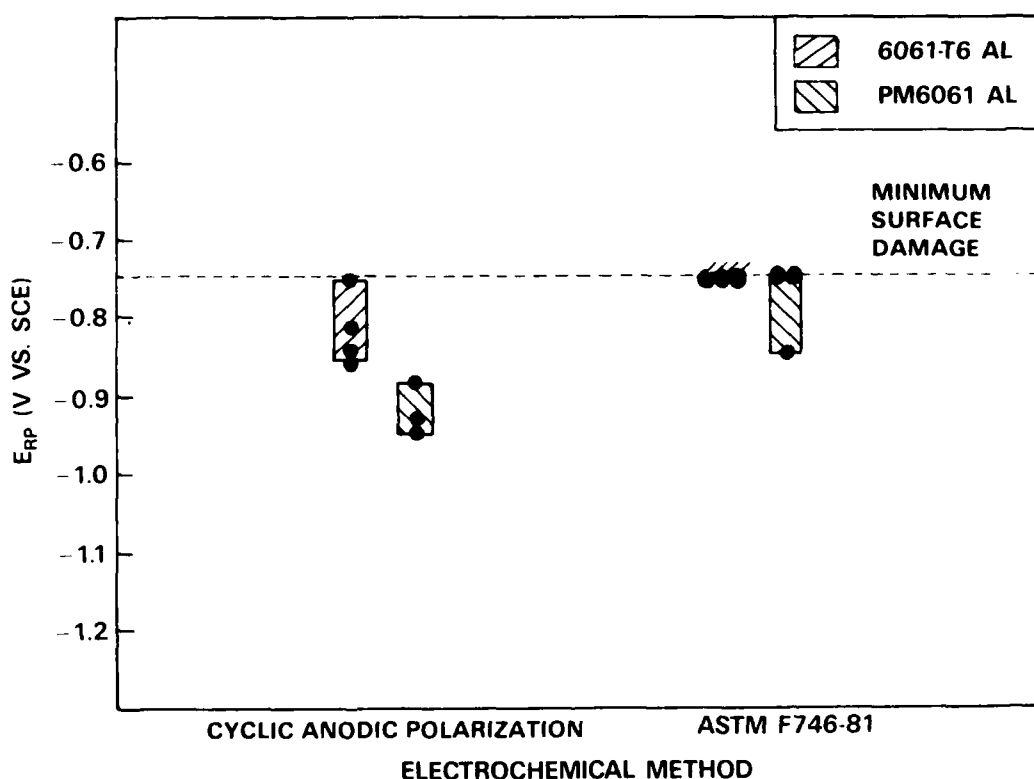
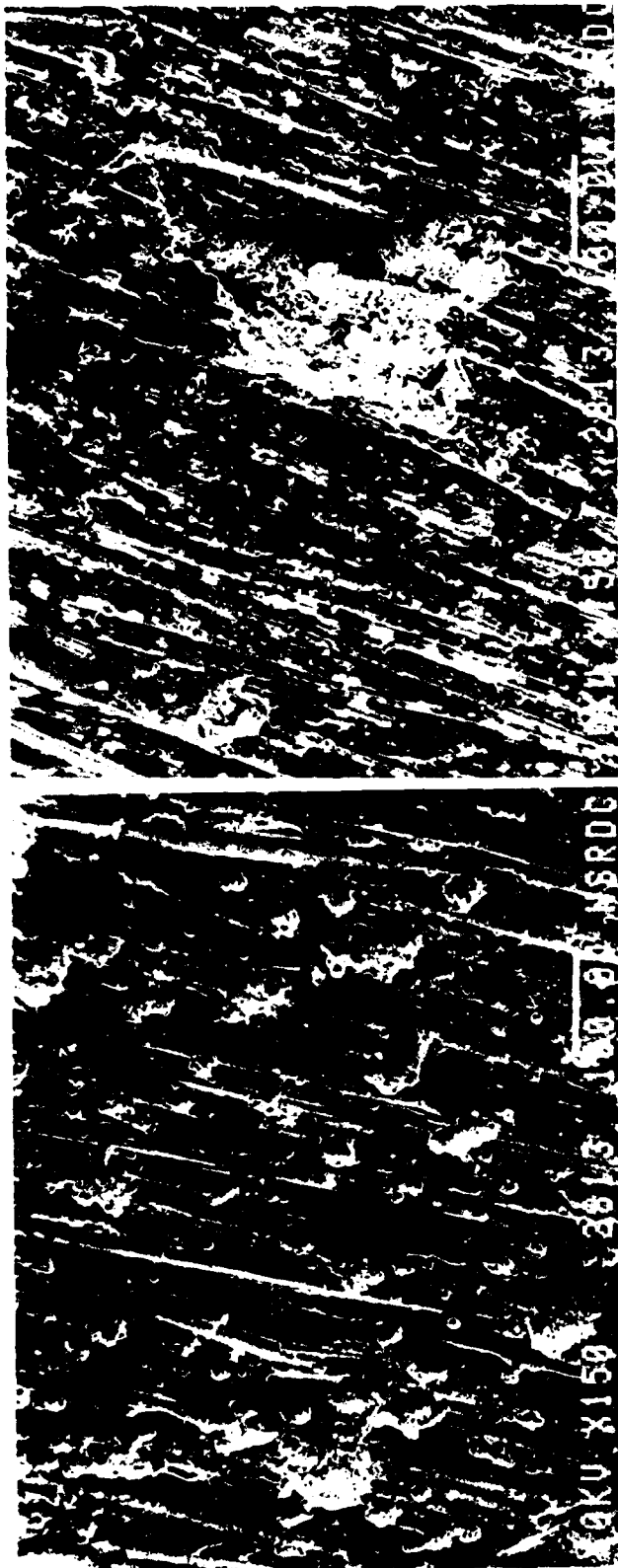


Figure 5 - Repassivation Potential Test Data for 6061-T6 Al and PM6061 Al Determined from Cyclic Anodic Polarization and ASTM Method F746-81



E_{pp} Determination
(ASTM F746-81)

E_{BD} Determination

(Also representative of specimen surfaces after cyclic anodic polarization and potentiostatic testing)

Figure 6 - 6061-T6 Al Pitting Morphology After Quasi-Stationary Anodic Polarization

Repassivation potentials determined for 6061-T6 Al by the CAP test (Figure 5) fall within the same range of values reported for wrought and PM6061 Al in the quasi-stationary anodic polarization method, suggesting that the amount of pit propagation was minimal for 6061-T6 Al in the CAP test. The E_{rp} range for PM6061 Al in the CAP test was significantly more electronegative than the other repassivation potentials, indicating a greater degree of pit propagation. Experimental procedure for the CAP method specifies a maximum current density to be reached before scan reversal. The degree of pit propagation on a particular specimen can vary depending on the amount of time it takes the specimen to reach that maximum current density level and return to the repassivation value. Thus, it is suggested that the CAP method would yield a more representative E_{rp} for a given material if the amount of coulombic charge per unit area were controlled (at a low level), thereby minimizing surface damage prior to E_{rp} determination.

For stainless steels, the repassivation potential after minimal pit growth is considered by Syrett¹⁶ to be the most representative repassivation potential since it closely simulates the conditions a passive metal surface would experience in service. Passive metals in marine applications initially have pit-free surfaces but undergo local events at the substrate/oxide film/water interfaces which are the precursor events to pit initiation and result in local changes in corrosion potential. Assuming that pitting will eventually initiate on a material in service, it is of practical value from a corrosion prevention viewpoint to know the potential at which repassivation will occur after minimal pit growth.

For breakdown potential determination by a potential-controlled electrochemical method, the E_{bd} is found by determining the potential at which the current increases. The specific value found depends on the time allowed for pit nucleation and growth to occur, as discussed earlier. Figure 7 presents the E_{bd} determined by several different methods on 6061 Al as a function of the residence time at the potential determined to be E_{bd} . Breakdown potential ranges from the cyclic anodic polarization method are also included, although the residence time allowed for pitting at each applied potential is not readily determined since CAP is a potentiodynamic test. However, with a CAP potential scan rate of 0.1 mV/sec it is estimated that the incubation time allowed for pitting is significantly less than ten minutes. The short time at each potential in the CAP test would not allow pitting to initiate at potentials near E_{rp} , where the incubation time is much longer than for more electropositive potentials.

As seen in Figure 7, E_{bd} values found using cyclic anodic polarization varied over an extensive scatter range, which contrasted the very reproducible breakdown potentials determined by the quasi-stationary anodic polarization method on 6061-T6 Al. Breakdown potentials for the latter method ranged from -0.674 V to -0.724 V versus SCE. Breakdown potentials for 6061-T6 Al in deaerated 0.1N sodium chloride solution reported by Trzaskoma, et al.²⁰ using potentiostatic polarization were -0.640 V versus SCE, in good agreement with the quasi-stationary anodic polarization method. PM6061 Al specimens potentiostatically polarized at -0.650 V all experienced a continual increase in current after an initial pit incubation period of about 10 minutes, indicating active pitting on the surfaces of these specimens. These results were reported in Figure 7 as the E_{bd} occurring at or electronegative to -0.650 V versus SCE.

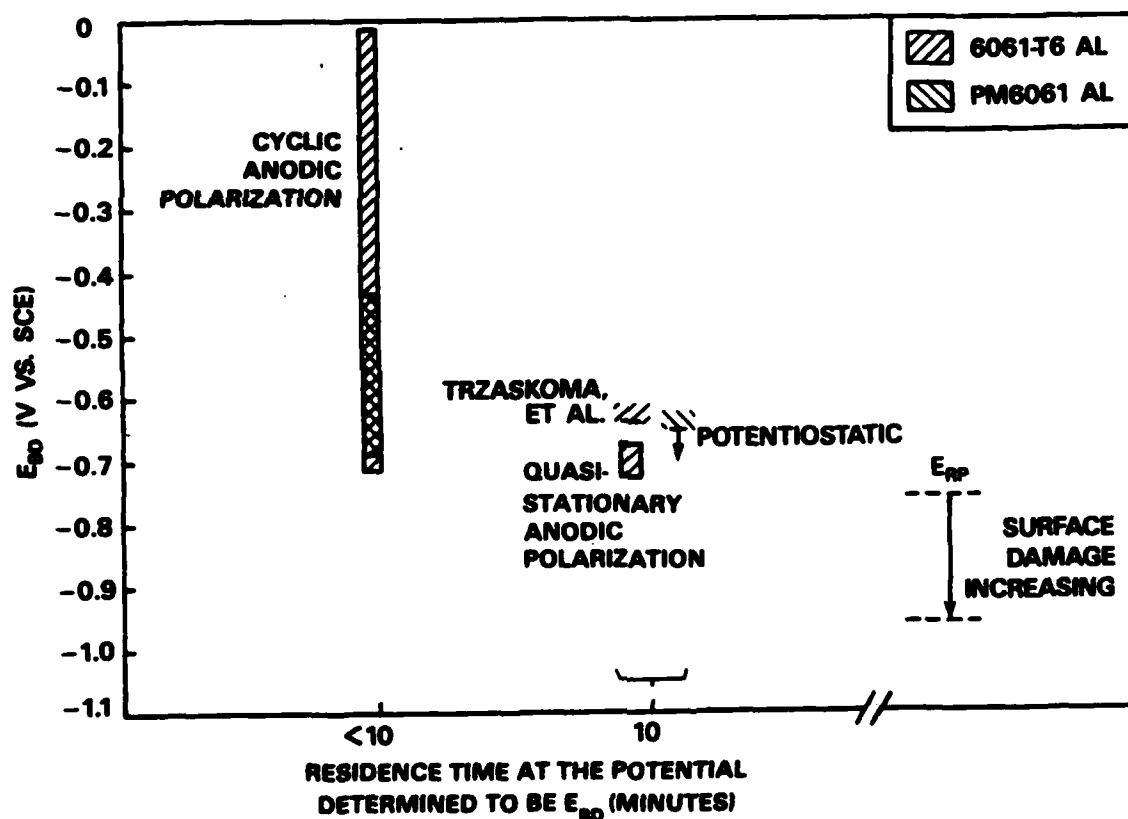


Figure 7 - Breakdown Potential Test Data for 6061-T6 Al and PM6061 Al Determined by Various Potential-Controlled Electrochemical Methods

E_{bd} values determined from the potentiostatic and quasi-stationary anodic polarization tests all fell in the electronegative end of the extensive range of E_{bd} values determined from cyclic anodic polarization. All of these potential-controlled tests are very dependent on an incubation time before pitting initiates, as discussed previously. Extending the pit incubation time to ten minutes at each applied potential in the quasi-stationary anodic polarization and potentiostatic methods increased the reproducibility of the E_{bd} parameter. The increased period of time at each applied potential also caused the breakdown potential to occur at a more electronegative potential.

The data in Figure 7 supports the assertion that the incubation time allowed for breakdown in any given test significantly influences the breakdown value. Shorter time allowances give rise to more electropositive and more irreproducible breakdown potentials. In comparing the electronegative trend in the breakdown potentials with the reported E_{rp} values, it can be seen that the most electronegative E_{bd} value is approaching the most electropositive E_{rp} value (corresponding to minimal surface damage). In fact, there is only a 26 mV difference in their potentials. An extension of this observation is that with sufficient time allowance, pitting will initiate at or slightly electropositive to E_{rp} . Thus, there exists only one characteristic potential for aluminum, E_{rp} .

PM6061 Al specimens with active pitting present on their surfaces after immersion in quiescent seawater for 14 months exhibited corrosion potentials of approximately -0.730 V versus SCE. These measured corrosion potentials are slightly electropositive to the E_{rp} value of -0.750 V versus SCE as determined from the quasi-stationary anodic polarization method and further support the theory of one characteristic potential for aluminum, above which active pitting will occur given a sufficient incubation period.

Proper determination of the characteristic potential E_{rp} can be accomplished utilizing either cyclic anodic polarization or the quasi-stationary anodic polarization method for E_{rp} determination. In the CAP test, care must be taken to minimize the extent of pitting attack subsequent to initiation. This can be achieved by minimizing the coulombic charge per unit area. The total charge per unit area before E_{rp} determination in the CAP test varied from 3-130 coulombs/cm². This large range is presumably related to reproducibility problems encountered during this test. The charge/unit area necessary to determine E_{rp} in the quasi-stationary anodic polarization method was determined to be significantly less

than 1 coulomb/cm². The procedure as specified in this method provides a reproducible E_{rp} value after minimal surface damage because the maximum current density allowed after pit initiation is quickly reached and the potential is then immediately shifted to a value closer to E_{rp} .

CONCLUSIONS

- The measured breakdown potential value for aluminum is significantly influenced by the incubation time allowed for pit initiation and growth, with longer time allowances giving rise to more electronegative and reproducible values.

- An extension of the previous conclusion, which has been postulated by other investigators as well, is that the repassivation potential is the only characteristic potential. That is, it is this potential below (electronegative to) which pitting is impossible and above which pitting will propagate subsequent to initiation.

- Cyclic anodic polarization can be used to obtain reproducible repassivation potentials; however, a more representative repassivation potential can be attained by minimizing surface damage after pit initiation through limitation of the amount of coulombic charge allowed per unit area.

- The quasi-stationary anodic polarization method outlined in ASTM F746-81 provides reproducible repassivation potentials and is a useful and relatively simple method for determining E_{rp} after minimal pit growth.

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